Catalytic activity of FeZSM-5 zeolites in benzene hydroxylation by N₂O: The role of geometry characterized by fractal dimensions

Melkon Tatlier [a], Lioubov Kiwi-Minsker [b],*

[a] *Department of Chemical Engineering, Istanbul Technical University, Maslak, 34469 Istanbul, Turkey*
[b] *Ecole Polytechnique Fédéral de Lausanne (LGRC-EPFL), CH-1015 Lausanne, Switzerland*

Abstract

The fractal dimensions of FeZSM-5 zeolites were used to characterize the change in their geometry depending on different post-synthesis treatments. The fractal dimension values were estimated from the Dubinin–Astakhov isotherms of nitrogen adsorption and related to the activity of these zeolites in the benzene hydroxylation to phenol by nitrous oxide. The zeolites had two different iron contents (350 and 5800 ppm) and a Si/Al ratio of 42. The catalysts were activated by steaming (823 K) and/or calcinations in He (1323 K). The FeZSM-5 activated by steaming exhibited fractal dimensions lower than the samples activated by calcinations. The steamed samples also had activities in the benzene hydroxylation per Fe(II) site (TOF values) somewhat higher as compared to the zeolites activated by calcinations. This indicates the importance of the zeolite geometry for the reaction of bulky benzene molecule within a confined space.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Iron containing ZSM-5 zeolites have been reported to be efficient catalysts for reactions involving N₂O: the stoichiometric decomposition of N₂O or its reduction with hydrocarbons, oxidation of methane to methoxy-species at low temperatures, and the hydroxylation of benzene to phenol with selectivity close to 100% and conversion of 50% [1–5]. The catalytic performance is due to iron in the zeolites [6–8]. The sites active in these reactions are formed during the zeolite pre-treatments by steaming and/or high temperature calcinations. It is believed that such activation leads to the extra-framework Fe(II) species stabilised via Fe–O–Al complexes in the zeolite micropores, which can interact with N₂O at 523 K, generating surface oxygen or so called "α-oxygen" species:

$$N_2O + (\ )_{Fe} = N_2 + (O)_{Fe} \tag{1}$$

This surface oxygen is responsible for zeolite activity in all the above mentioned reactions involving N₂O.

In a previous publication of some of us, a variety of Fe-containing ZSM-5 catalysts were prepared by different methods and tested for activity in benzene hydroxylation by N₂O [9]. The total Fe content in the zeolites ranged from 0.015 to 2.1 wt%. The catalysts were activated by steaming and/or high temperature treatment in He (1323 K). The Fe(II) sites formed in the zeolites were characterized quantitatively by the transient response method in the low temperature N₂O decomposition according to reaction (1). The formation of surface atomic oxygen was followed by the transient response in CO oxidation by the surface (O)_{Fe} pre-loaded from N₂O. This approach allowed to determine the amount of total Fe(II) sites

involved into the reaction (1) and the amount of sites with the surface oxygen species active in CO oxidation. The activity in benzene hydroxylation was observed to correlate with the amount of Fe(II) sites active in CO oxidation, but the TOF values varied depending on the zeolite pretreatment conditions. This reflects the complexity of the system that not only the presence of Fe(II) site may be important for the reactivity, but also the accessibility of active $(O)_{Fe}$ for the bulky benzene molecule and benzene activation. The observed activity is influenced by the zeolite morphology and microporous structure depending on the post-synthesis treatment (steaming, calcinations, etc).

Fractal geometry is useful for the characterization of the surface irregularities of solid materials. The fractal dimension allows to measure the degree of roughness of a solid by evaluating how fast the measurement results change as the scale becomes larger or smaller. An object having a non-integer dimension ($D \neq 1, 2, 3$) is fractal. The variation of the monolayer capacities for different gas molecules in an isotropic series with respect to the size of the molecules enables the evaluation of the fractal dimension of adsorbents/catalysts [10]. A fractal adsorbent/catalyst has an accessible surface area that decreases or increases with the increasing dimensions of the adsorbate molecules, for fractal dimension above and below 2, respectively. Fractal dimension above 2 means that the smaller molecules have access to the adsorption sites (or adsorbent/catalyst surface) not available for larger molecules. Fractal dimensions below 2 indicate that the larger molecules can make use of the surface otherwise unavailable, by partly or completely covering them while they snap to the adsorption sites nearby. The smaller molecules do not have such an opportunity since they are not large enough. When the fractal dimension is equal to 2, the same amount of surface area is available for molecules of different sizes. The determination of the fractal nature of zeolites may be of crucial importance for the prediction of the scaling behavior encountered in catalysis. The geometric shapes of the pore surfaces and the relative proximity of the molecule sizes to the structural building units are mainly responsible for the fractality of zeolite catalysts. When treatments, such as high-temperature calcinations and steaming are applied to the zeolite, the pore size distribution in the modified catalyst becomes important. A wider pore size distribution indicates the presence of a higher fractal dimension, which may exceed 2. It has been demonstrated that the fractal dimension can be estimated from isotherms [11–13]. One of these methods is based on the Dubinin–Astakhov (D–A) equation and uses two adsorption isotherms, one of them pertaining to the investigated adsorbent and the other to the reference adsorbent, the fractal dimension of which is already available [13].

The investigation of the morphology changes is important since the modified geometry of the zeolite may lead to changes in the adsorption and diffusion properties of these materials. The catalytic performance is also known to be affected by the geometrical details of the catalyst in many cases [14]. Fractal analysis is a tool to characterize the zeolites and describes the changes occurring in the parent zeolite due to post-synthesis treatment. It has been observed that the fractal dimensions of synthetic zeolite NaY may vary significantly after being subjected to different post-synthesis treatments, such as chemical dealumination, ultrastabilization and realumination [15].

In this study, the fractal dimensions of FeZSM-5 zeolites containing two different amounts of iron, but the same Si/Al ratio, were estimated after different activation procedures. The D–A method and the nitrogen adsorption isotherms of the zeolites were used. The validity of using nitrogen in the D–A method was tested by comparing the fractal dimensions of zeolites with the values reported in literature. The relations of the fractal dimension with the TOF values determined for the benzene hydroxylation to phenol are discussed.

2. Theory

The Dubinin–Astakhov isotherm equation may be expressed as

$$w = w_0 \exp(-(A/E)^n), \tag{2}$$

where w and w_0 represent the number of moles and the total amount of pore filling, respectively. E is the characteristic energy of adsorption and n is a dimensionless parameter (geometric factor). The differential molar work of adsorption (A) may be expressed as

$$A = RT \ln(P_s/P), \tag{3}$$

where P_s is the saturation pressure. The geometric factor (n) has been shown to be related to the fractal dimension (D) in the form

$$n = (3 - D)/c, \tag{4}$$

where c is a constant characteristic of the adsorbate used [13]. In order to estimate the fractal dimension of the adsorbent using the D–A method, the n value of the adsorbent and that of the reference adsorbent should be utilized. Once the constant c characteristic of the adsorbate is calculated, the fractal dimension of the adsorbent can be determined.

The adsorbates that have been tested up to now by using the D–A method were: methane, ethane, propane, ethylene, propylene and methanol [13]. The fractal dimensions of the zeolites 13X, 5A, 4A and silicalite (with structure similar to ZSM-5) have been calculated in previous studies [12,13]. In this study, the adsorption isotherm of zeolite 13X ($D = 2.13$) is used as the reference adsorbent.

As the first step in the calculation of the fractal dimension, the values of the parameters E, w_0 and n were calculated by the Levenberg–Marquardt algorithm which finds the values of the coefficients that give the best fit between the equation and the data. The Levenberg–Marquardt algorithm is an iterative procedure that uses a nonlinear least-squares technique. Then, the fractal dimensions of zeolites 5A and ZSM-5$_{350}$ were estimated to verify the suitability of using nitrogen in the D–A method. Finally, the fractal dimensions of the activated FeZSM-5 catalysts were estimated. The relationship between the fractal dimensions of the FeZSM-5 samples and the TOF values of benzene hydroxylation to phenol by nitrous oxide, calculated as reaction rate per Fe(II) site active in the CO oxidation [9] is discussed.
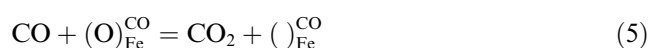
3. Experimental

Nitrogen adsorption isotherms were determined for eight different samples, namely for commercial 13X and 5A zeolites and six FeZSM-5 catalysts reported previously [9]. The adsorption experiments were performed at 77 K by using a Sorptomatic 1990 instrument (Carlo Erba). Prior to the experiments, the zeolites were kept at 523 K in vacuum for 2 h.

The Si/Al ratio of the ZSM-5 samples investigated was equal to 42 and these zeolites had two different iron contents of 350 and 5800 ppm. The isomorphously substituted ZSM-5 samples had been prepared by hydrothermal synthesis and was activated by steaming (H_2O partial pressure of 0.3 bar; He flow rate 50 ml/min) at 823 K for 4 h or by calcinations in a He flow (50 ml/min) at 1323 K for 1–11 h [9]. The steamed samples are denoted by ZSM-5$_{350s}$ or ZSM-5$_{5800s}$ while the calcined samples are represented by ZSM-5$_{350c}$, ZSM-5$_{5800c}$ or ZSM-5$_{5800c11}$. For ZSM-5$_{350c}$ and ZSM-5$_{5800c}$ calcinations had performed for 1 h while this period was extended to 11 h for ZSM-5$_{5800c11}$. One of the ZSM-5 samples (ZSM-5$_{350}$) was not activated but only calcined in air at 823 K to remove the organic template.

The determination of the Fe(II) sites in the ZSM-5 samples as well as the testing of the catalysts during the benzene hydroxylation with N_2O was reported in previous publication [9].

As the first step, the formation of surface oxygen $(O)_{Fe}$ from N_2O was carried out by introducing into the reactor as a mixture of 2 vol% N_2O + 2 vol% Ar + 96 vol% He. Then the deposited oxygen $(O)_{Fe}^{CO}$, which is active in CO oxidation at low temperature (553 K), was measured via the transient response of CO_2 during CO oxidation performed immediately after the sample treatment by N_2O at 553 K (deposition of $(O)_{Fe}$) according to the reaction:

$$CO + (O)_{Fe}^{CO} = CO_2 + (\ )_{Fe}^{CO} \qquad (5)$$

The concentration of the corresponding Fe(II) sites – C_{Fe}^{CO} – was determined assuming that one active oxygen atom can attach to one Fe(II) site. During the measurements, the gas phase was monitored in the reactor outlet after switching in the inlet from He to a mixture 3 vol% CO + 97 vol% He. The C_{Fe}^{CO} was determined by integration of the CO_2 peak. This method has been described elsewhere [16,17].

Benzene hydroxylation was carried out in a vertical stainless-steel fixed-bed reactor (inner diameter – 20 mm) at 510–600 K and atmospheric pressure. The catalyst ($m = 0.3$–1.0 g, $d_p = 0.2$–0.5 mm) was placed on a plate of sintered stainless-steel fibers, which was fixed in the middle of the reactor. The catalyst was mixed with inert silica grains to form a uniform catalyst bed of 3–4 mm height. The mixture of 1 vol% of benzene, 5 vol% of N_2O and 94 vol% of He was used for the catalytic tests at a gas flow of 60 ml (STP)/min.

4. Results and discussion

4.1. Estimation of the fractal dimension

The nitrogen adsorption isotherms of the zeolites 13X and 5A are shown in Fig. 1(a) while those of ZSM-5$_{350}$, ZSM-5$_{350s}$, ZSM-5$_{350c}$, ZSM-5$_{5800s}$, ZSM-5$_{5800c}$ and ZSM-5$_{5800c11}$ Fe-zeolites are shown in Fig. 1(b). It is difficult to conclude from the shapes of the isotherms, alone, if a structural change in the activated FeZSM-5 samples is taking place or not. Fractal analysis allows the accomplishment of a more detailed investigation. The fractal dimensions of the zeolites were estimated by using the Dubinin–Astakhov method and nitrogen as the adsorbate [13]. As mentioned before, zeolite 13X was employed as the reference adsorbent.

It is certain that a good fit of the adsorption data to the D–A equation, especially at the stage near monolayer coverage, is required if a reflection of the fractal dimension should be expected [13]. Thus, as a first step in the calculations, the variation of the geometric factor (n) with the adsorption pressure was investigated. The variation of the n values with respect to p_{min}, which represents the lowest pressure value in the pressure range employed to estimate n, is shown in Fig. 2 for the zeolites 13X and 5A. The high pressure value was kept constant at about 500 torr. The n values varied significantly in the pressure range used to estimate the Dubinin–Astakhov isotherm equation parameters. As p_{min} was increased, the n values first decreased followed by an increase. In order to determine the pressure range in which the adsorption data fitted the Dubinin–Astakhov isotherm equation the difference between the experimental and predicted number of moles adsorbed was calculated for different parts of the isotherms. The minimum deviation of the number of moles predicted by the D–A
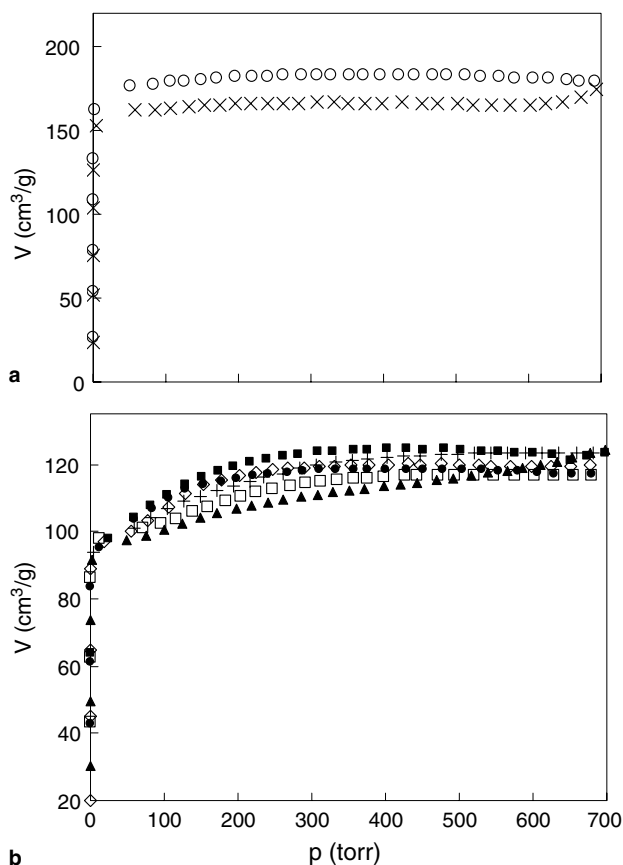
Fig. 1. Nitrogen adsorption isotherms of the zeolites: (a) (X) 13X, (○) 5A, (b) (●) ZSM-5$_{350}$, (◇) ZSM-5$_{350s}$, (□) ZSM-5$_{350c}$, (■) ZSM-5$_{5800s}$, (+) ZSM-5$_{5800c}$ and (▲) ZSM-5$_{5800c11}$.
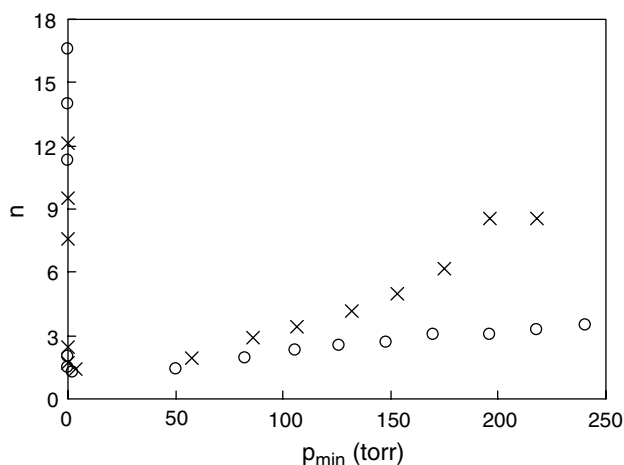

Fig. 2. Variation of *n* values with respect to p_{min}, which represents the lowest pressure value in the pressure range employed to estimate *n*, for the zeolites (×) 13X and (○) 5A .

Table 1
The fractal dimensions (*D*) of 5A and FeZSM-5 zeolites determined by using the Dubinin–Astakhov method and nitrogen as the adsorbate

Zeolite	*D*
13X	2.13 (ref.)
5A	2.16
FeZSM-5$_{350}$	1.59
FeZSM-5$_{350s}$	1.33
FeZSM-5$_{350c}$	1.60
FeZSM-5$_{5800s}$	1.40
FeZSM-5$_{5800c}$	1.66
FeZSM-5$_{5800c11}$	2.37

350 and 5800 represent the iron content of the catalyst in ppm while s and c denote activation by steaming and calcinations, respectively.

determine the fractal dimensions of the zeolites. The constant *c* in Eq. (4) for nitrogen was found to be 0.5138 using the fractal dimension of 13X already reported ($D = 2.13$) [12,13].

The fractal dimensions calculated for the zeolites 5A and ZSM-5$_{350}$, ZSM-5$_{350s}$, ZSM-5$_{350c}$, ZSM-5$_{5800s}$, ZSM-5$_{5800c}$ and ZSM-5$_{5800c11}$ Fe-zeolites are listed in Table 1. The fractal dimensions of LTA and MFI zeolites were estimated by using various adsorbates. The fractal dimensions of silicalite, 5A and 4A had been determined to be equal to 1.68 [12,13], 2.08 [12,13] and 2.15 [13], respectively. Zeolites 5A and 4A both have LTA structure, differing only in their cations. Silicalite and ZSM-5$_{350}$ both have MFI structure while they differ in their Si/Al ratios. Thus, the fractal dimensions of the zeolites 5A and ZSM-5$_{350}$ may be expected to be close to those of zeolites 4A and silicalite, respectively. The fractal dimensions of zeolite 5A and ZSM-5$_{350}$ found in this study were consistent with the values reported previously for zeolites with similar structure. Therefore, nitrogen can be used in the estimation of the fractal dimension by the Dubinin–Astakhov method. This shows that inorganic adsorbates, can be utilized in the Dubinin–Astakhov method as long as accurate adsorption measurements can be carried out, especially in the high pressure range. Larger molecules used in the estimations introduce loss in the accuracy of the results. Nitrogen, which is a small molecule, seems to be a good choice. The suitability of using nitrogen in the estimation of the fractal dimension by the Dubinin–Astakhov method allow this method to be widely used since nitrogen is one of the most commonly employed gases in the laboratories. The precision of the estimations may be increased further by using higher number of adsorption data.

It may be observed from Table 1 that the fractal dimensions of the activated ZSM-5 catalysts show some changes with respect to the inactivated ZSM-5$_{350}$ sample. Steaming carried out for 4 h at 823 K led to an observable decrease in the fractal dimension of the parent zeolite. But calcinations at 1323 K for 1 h lead to a slight enhancement of the fractal dimension. This increase became obvious and the fractal dimension exceeded 2 when

equation from the experimental values was ∼3%, and the best fit was obtained in the pressure range of 0.02–500 torr for zeolites 13X, 5A and in the range of 100–500 torr for the ZSM-5 samples. The *n* values obtained in these pressure ranges were employed in Eq. (4) to

the calcination was performed for 11 h. For the samples investigated, the iron content is not expected to have a significant impact on the fractal dimension of the ZSM-5 zeolite since the amount of iron in the zeolite is low. Additionally, the fractality of zeolites is mainly determined by the geometrical shapes of the pores and structural building units of these materials. The effect of the type of the T (Si, Al, Fe, etc.) atoms in the frameworks of zeolites on the fractal dimension is minor.

The specific surface and mesopore areas of the FeZSM-5 zeolites were estimated using the BET and t-plot methods, respectively. The specific surface areas of the steamed and calcined samples were observed to increase and decrease slightly with respect to the inactivated ZSM-5_{350} zeolite. The amount of change varied between 4% and 8% of the total surface area of ZSM-5_{350}. The amount of mesopores in ZSM-5_{350} increased when calcinations were applied, especially for the ZSM-$5_{5800c11}$ sample, while no significant change could be observed after steaming. The changes occurring in the micropore area (specific surface area-mesopore area) of the ZSM-5_{350} zeolite when steaming and calcinations were applied amounted to about 3–17% of the original area. The decrease and increase observed in the fractal dimension of the parent FeZSM-5 zeolite when steaming and calcinations were applied may be partly related to the changes occurring in the surface areas of the activated samples.

4.2. Relation of fractal dimension with catalyst activity in benzene hydroxylation

It had been previously demonstrated that the reaction rate of benzene hydroxylation varied linearly with the amount of Fe(II)-sites in the isomorphously substituted FeZSM-5 active towards CO oxidation [9] as shown in Fig. 3. But some minor deviations from direct propor-
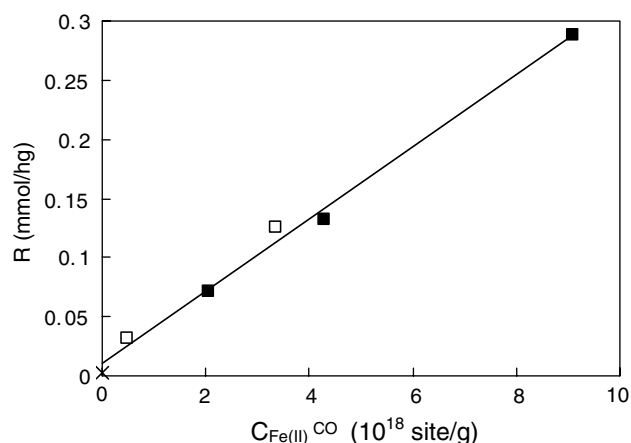

Fig. 3. Relationship between the concentration of Fe(II) sites and the reaction rate of benzene hydroxylation when CO oxidation was used for the measurement of the Fe(II) sites in ZSM-5 catalysts: (■) calcined, (□) steamed and (×) not activated.
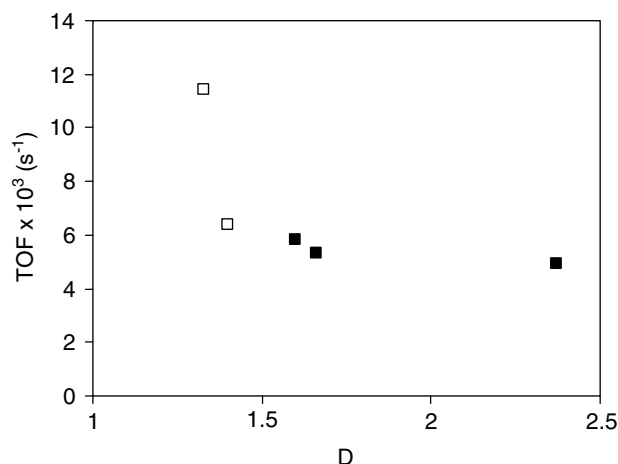

Fig. 4. Relationship between the fractal dimensions of FeZSM-5 catalysts and the TOFs obtained for the benzene hydroxylation when (■) calcined and (□) steamed zeolites were used.

tionality have also been observed. The both zeolites ZSM-5_{350s} and ZSM-5_{5800s} activated by steaming exhibited TOFs about 20–50% higher as compared to the same samples activated by calcinations [9]. The fractal dimensions of the steamed samples were lower than those of the other ZSM-5 catalysts. Fig. 4 shows the relationship between the fractal dimensions of the treated FeZSM-5 zeolites and the TOFs obtained for the benzene hydroxylation reaction by using these catalysts. For D values smaller than about 1.6, which represents the fractal dimension of the untreated ZSM-5 sample, the TOFs increased as the fractal dimension decreased. For D values larger than about 1.6 the TOFs remained relatively constant. Decreasing the fractal dimension of the catalyst below its initial value may be a good choice for increasing the TOFs in the benzene hydroxylation reaction. Steaming seems to have accomplished this task. Increasing the fractal dimension above the initial value of the zeolite by calcinations was ineffective. It should be reminded that the amount of the Fe(II)-sites formed in the FeZSM-5 as a result of the post-synthesis treatment is also important for the catalytic activity.

The fractal dimension is an indicator of the size sensitivity of solid materials. As the fractal dimension gets lower, the amount of the accessible surface area of the catalyst increases for benzene compared to CO. Since the fractal dimension of the steamed sample was determined to be lower compared to the calcined and original samples, this brings a geometrical advantage for the reactivity of large benzene and/or desorption of phenol molecules. The decrease in the fractal dimensions of the steamed samples may be related to the increase in the surface area, possibly due to formation of Si–O bonds on the surface. This allowed the use of the iron sites in the zeolite for the benzene molecules, resulting in higher TOF values. The observation that a significant change in TOF values was not obtained for the calcined samples,

which had higher fractal dimensions if compared to the original ZSM-5, may indicate that the number of iron sites in the catalysts was the main factor determining activity. It seems that the smaller amount of accessible (micropore) surface area and the presence of mesopores did not affect the use of the iron sites in the zeolite. The results signify that for the steamed FeZSM-5 samples the changes occurring in the geometry and surface area of the zeolite played a role in the reaction of benzene hydroxylation besides the active Fe(II)-sites.

Lower values of TOFs obtained for the calcined samples if compared to the TOFs of steamed samples may also be due to smaller amount of hydroxyl groups on the zeolite surface. These groups are important for the zeolite activity together with the presence of Fe(II) sites [18,19], being responsible for the benzene activation. A detailed kinetic study was carried out previously varying the reactant concentrations, benzene/N_2O ratio and residence time [20]. The results obtained suggested a surface reaction between benzene and atomic oxygen adsorbed on two neighboring active sites. Therefore, dehydroxylation taking place during high temperature calcination in He may also be responsible for the lower TOFs observed. Interesting is that the high fractal dimension of the ZSM-$5_{5800c11}$ sample obtained after calcinations for 11 h at 1323 K, did not lead to a significant decrease in the TOF number compared to the same sample after calcinations for 1 h. It may be concluded that besides the smaller fractal dimension, the creation of some Brönsted sites during the activation by steaming increases the zeolite activity. It should be remembered that the significance of the geometrical effect may differ depending of the reaction, as well as for ZSM-5 samples with different Si/Al ratios and for different preparation/activation conditions. Thus, more work should be performed in this respect for reaching a more complete conclusion.

5. Conclusion

A good fit of the adsorption data to the Dubinin–Astakhov equation allowed to estimate the fractal dimensions of the 5A and FeZSM-5 zeolites. Nitrogen was shown to be suitable as adsorbate. The pressure range allowing the most precise determination of the parameters of the Dubinin–Astakhov equation should be used for the estimations. The fractal dimensions of the FeZSM-5 catalysts, activated by steaming at 823 K were lower than those of the FeZSM-5 samples after calcinations at 1323 K in He. The lower fractal dimensions of the steamed zeolites reflect a better geometry for bulky benzene molecule if compared with the calcined zeolites possessing higher fractal dimensions. High amount of Brönsted active sites may also contribute to the higher TOFs obtained for the steamed catalysts.

References

[1] V.I. Sobolev, K.A. Dubkov, E.A. Paukshtis, L.V. Pirutko, M.A. Rodkin, A.S. Kharitonov, G.I. Panov, Appl. Catal. A 141 (1996) 185.
[2] K.A. Dubkov, V.I. Sobolev, E.P. Talsi, M.A. Rodkin, N.H. Watkins, A.A. Shteinman, G.I. Panov, J. Mol. Cat. A 123 (1997) 155.
[3] G.I. Panov, A.K. Uriarte, M.A. Rodkin, V.I. Sobolev, Catal. Today 41 (1998) 365.
[4] J.A.Z. Pieterse, S. Booneveld, R.W. van den Brink, Appl. Catal. B 51 (2004) 215.
[5] G.D. Pirngruber, M. Luechinger, P.K. Roy, A. Cecchetto, P. Smirniotis, J. Catal. 224 (2004) 429.
[6] V.I. Sobolev, G.I. Panov, A.S. Kharitanov, V.N. Romannikov, A.M. Volodin, K.G. Ione, J. Catal. 139 (1993) 435.
[7] Q. Zhu, B.L. Mojet, R.A.J. Janssen, E.J.M. Hensen, J. Van Grondelle, P. Magusin, R.A. van Santen, Catal. Lett. 81 (2002) 205.
[8] K.A. Dubkov, N.S. Ovanesyan, A.A. Shteinman, E.V. Starokon, G.I. Panov, J. Catal. 207 (2002) 341.
[9] I. Yuranov, D.A. Bulushev, A. Renken, L. Kiwi-Minsker, J. Catal. 227 (2004) 138.
[10] P. Pfeifer, D. Avnir, J. Chem. Phys. 79 (1983) 3558.
[11] D. Avnir, M. Jaroniec, Langmuir 5 (1989) 1431.
[12] M. Tatlier, A. Erdem-Senatalar, J. Phys. Chem. B 103 (1999) 4360.
[13] A. Erdem-Senatalar, M. Tatlier, A. Sirkecioglu, Coll. Surf. A 173 (2000) 51.
[14] D. Farin, D. Avnir, J. Am. Chem. Soc. 110 (1988) 2039.
[15] B. Sulikowski, J. Phys. Chem. 97 (1993) 1420.
[16] L. Kiwi-Minsker, D.A. Bulushev, A. Renken, J. Catal. 219 (2003) 273.
[17] L. Kiwi-Minsker, D.A. Bulushev, A. Renken, Catal. Today 91–92 (2004) 165.
[18] P.P. Notte, Top. Catal. 13 (2000) 387.
[19] P. Kubanek, B. Wichterlova, Z. Sobalik, J. Catal. 211 (2002) 109.
[20] B. Louis, L. Kiwi-Minsker, P. Reuse, A. Renken, Ind. Eng., Chem. Res. 40 (2001) 1454.